

Digitally alloyed ZnO and TiO₂ thin film thermistors by atomic layer deposition for uncooled microbolometer applications

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Digitally alloyed ZnO and TiO₂ thin film thermistors by atomic layer deposition for uncooled microbolometer applications

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The authors demonstrate the digital alloying of ZnO and TiO₂ via atomic layer deposition method to be utilized as the active material of uncooled microbolometers. Depositions are carried out at 200 °C. Crystallinity of the material is shown to be degraded with the increase of the Ti content in the grown film. A maximum temperature coefficient of resistance (TCR) of −5.96%/K is obtained with the films containing 12.2 at. % Ti, and the obtained TCR value is shown to be temperature insensitive in the 15–22 °C, thereby allowing a wide range of operation temperatures for the low cost microbolometers. © 2017 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4976513>]

I. INTRODUCTION

Uncooled microbolometers are popular in infrared imaging due to their compactness, low-cost, and CMOS compatibility.¹ The temperature sensitive active material is a critical component of resistive type microbolometers. The resistance of the active material changes in response to increasing temperature due to infrared radiation.² Most widely used active materials are amorphous Si,³ VO_x,⁴ YBaCuO,⁵ and polycrystalline Si-Ge (Ref. 6) among which VO_x is widely accepted as the gold standard due to its high temperature coefficient of resistance (TCR) with 2–3%/K. However, VO_x is not compatible with CMOS technology, making integration costly.⁷ Recently, alternative materials have been sought after to improve the performance of the microbolometers while decreasing the manufacturing costs. One of these materials is ZnO, which has been deposited using several methods, including pulsed laser deposition,⁸ sputtering,⁹ and atomic layer deposition (ALD).¹⁰ Among these methods, ALD-deposited ZnO produced the most promising results with thin films having TCR values as high as −10.4%/K. Despite such a high TCR value, ZnO films suffer from poor electrical stability.^{11,12} Compared to ZnO, TiO₂ presents a more stable alternative owing to more negative standard energy, according to the Ellingham diagram of oxides.¹³ In a recent work, TiO₂ is shown to possess a maximum TCR value of −9%/K.¹⁴ However, in the same study it is observed that the TCR of the TiO₂ is temperature dependent. Therefore, an electrically stable material with high and temperature insensitive TCR is desired.

In this work, digital alloying of ZnO and TiO₂ thin films deposited via ALD is shown to possess stable and high TCR values and reduced dependency on the operating temperature. Structural and elemental characterization of the films is performed for Ti concentrations varying from 2.5% to 12.2%. The temperature dependent electrical characteristics of the films are also studied and the Ti-ZnO (TZO) digital alloy is offered as a promising microbolometer active material compromising high TCR with the temperature independent operation capability.

II. EXPERIMENT

A. Materials characterization

The chemical state of each constituent and elemental composition of the deposited films in their bulk forms were determined by depth profile analysis using a beam of Argon ions having 1 kV energy and 400 μm spot size (Thermo Scientific X-ray Photoelectron Spectroscopy Al Kα). For the structural analysis of the ALD based TZO films, PANalytical X'Pert PRO Materials Research Diffractometer is operated at 45 kV and 40 mA with the Cu Kα x-ray source.

Deposited TZO films were subjected to XPS analysis of Zn 2p, Ti 2p, and O 1s to determine the chemical state of elements in the films. Three different doping levels were studied and advantageous C fit was applied for all samples by setting C 1s peak to 284.8 eV for internal charge correction. Figure 1 shows the core level Zn 2p, Ti 2p, and O 1s XPS spectra of TZO films with 12.2% Ti concentration (see supplementary material²⁵).

Zn 2p_{3/2} core level spectrum of TZO films with 12.2% Ti concentration was fitted with a subpeak having a binding

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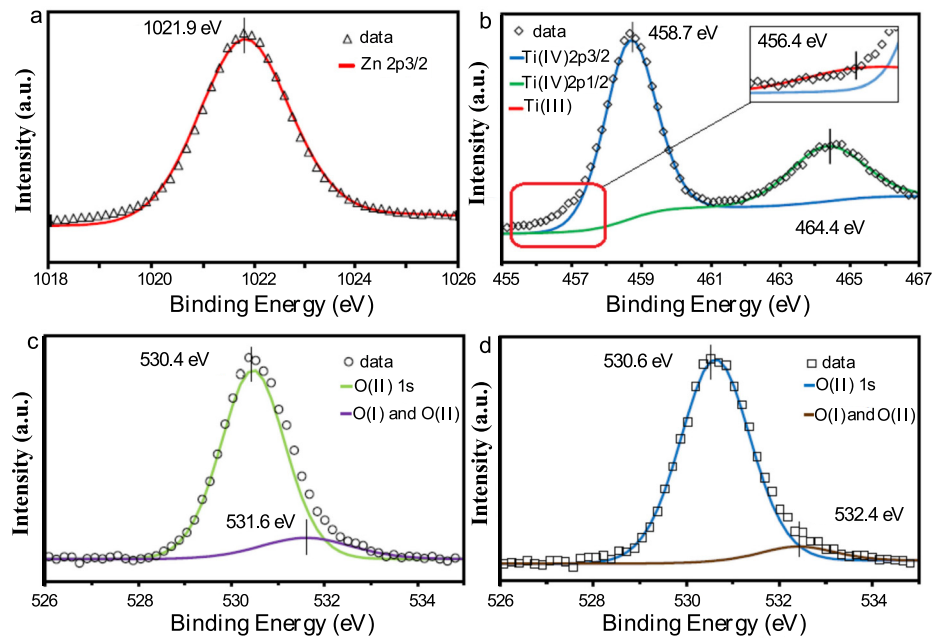


FIG. 1. (Color online) Core level XPS spectra of the TZO film with 12.2% Ti concentration: (a) Zn 2p_{3/2}, (b) Ti 2p, (c) O 1s, Zn (II), and (d) O 1s, Ti (IV).

energy of 1021.9 eV which matches with the Zn–O bond in the literature.¹⁵ Ti 2p core level spectrum of TZO with 12.2% Ti concentration was deconvoluted into three peaks which corresponds to 2p_{3/2}, 2p_{1/2}, and Ti (III) ions as illustrated in Fig. 1(b). The spectral positions of peaks are 458.7, 464.4, and 456.4 eV which are in good agreement with various studies.^{16–18} Ti (III) ions were only observed for TZO with 12.2% Ti concentration which shows loosely ordered structure as proved by structural characterization. Also, the symmetric shape of peaks, spin orbit splitting value of 5.7 eV for TiO₂, and the intensity ratio of the 2p_{3/2} and 2p_{1/2} peaks which is 2:1 are consistent with the literature.¹⁹ From Ti 2p XPS spectra of TZO film with 12.2% Ti concentration, it is clear to say that Ti is present in TZO films in an oxide form rather than a metallic form.

Although it is hard to distinguish O (II) state of ZnO and TiO₂ from O 1s core level spectrum, the peak energy values of adsorbed ions at lattice defect sites of ZnO and TiO₂ provide the clear identification of them. For ZnO, chemisorbed O[–], O[–] ions cause the occurrence of a minor peak with a spectral location at 531.6 eV. As seen from Fig. 1(c), the major peak centered at 530.4 eV refers to Zn–O bond and the minor peak with a spectral location at 531.6 eV corresponds to chemisorbed oxygen. Table I shows the atomic concentrations and ratios of minor peak to major peak of

deposited three different TZO films. It is observed that, as Titanium concentration increases in TZO films, the ratio of minor peak, which is oxygen related defect peak, to Zn–O major peak decreases. This shows the reduction in oxygen related defects. On the other hand, for TiO₂, it is known that adsorbed ions like –OH, –CO, O₂, H₂O, produce a minor peak at 532.4 eV.²⁰ Similarly, subpeaks with binding energies at 530.5 and 532.4 eV are attributed to O (II) in TiO₂ and adsorbed ions as illustrated in Fig. 1(d). The subpeak with a spectral location at 532.4 eV is only observed for TZO with 12.2% Ti concentration.

Figure 2 shows the grazing incidence x-ray diffraction spectra of TZO samples. The experiments were performed with 0.05 step size and 5 s counting time for all samples. Pure ZnO film deposited at 200 °C with ALD was used as a reference material. Hexagonal wurtzite ZnO phase was observed and any phase related to Zn or Ti cannot be

TABLE I. Atomic concentrations and ratios of minor peak to major peak of deposited TZO films.

Sample	Atomic percentage				Minor to major peak ratio
	Zn	O	Ti	Ar	
1	49.4	46.3	2.5	1.8	1:6
2	45.3	47.3	5.9	1.5	1:18
3	33.1	53.2	12.2	1.5	1:28

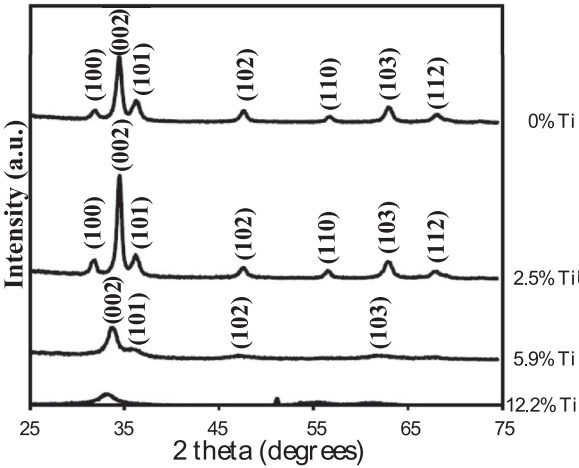


FIG. 2. Grazing incidence x-ray diffraction analysis of TZO films.

detected as seen from Fig. 2. In ZnO and its related compounds, it is natural to observe preferred orientation in (002) direction (c axis).²¹ Also, it is obvious that, as titanium concentration in the film increases, broad peaks with low intensity are obtained indicating distorted crystal structure as reported in the literature.^{22,23}

B. Device fabrication

Interdigitated microresistors are fabricated to electrically characterize the synthesized material. Fabrication of the resistor starts with the standard RCA cleaning of the silicon wafer. A 200-nm-thick SiO₂ insulation layer is deposited via electron beam evaporation. This is followed by ALD growth of TZO at 200 °C. Depositions of titanium doped ZnO films were carried out at 0.15 Torr chamber pressure and 200 °C in a Savannah S100 ALD reactor. Mili-Q water and organometallic precursor diethylzinc were used for ZnO deposition. The pulse time of 0.015 s was used for both the organometallic precursor and water. Nitrogen was used as purge gas with a flow rate 20 sccm and purge time was 10 s. Under these conditions, the growth rate of the ZnO was determined as 0.12 nm/cycle. Tetrakis(dimethylamido)titanium (preheated to 75 °C) and mili-Q water were used as the precursors for Titanium doping. Pulse durations of water and organometallic precursor were 0.015 and 0.1 s, respectively. Purge gas was nitrogen with a flow rate 20 sccm and purge period was determined as 10 s for both of the precursors. The growth rate of the TiO₂ was found as 0.04 nm/cycle. Different ratios of ZnO:TiO₂ subsycles (5:1), (5:2), (5:3) were repeated 50 times and finally TZO thin films with 2.5%, 5.9%, and 12.2% Titanium concentrations were obtained, respectively. The thicknesses of TZO films were determined as 32, 34, and 36 nm using a mechanical profilometer (Stylus KLA Tencor P-6). Finally, ohmic contacts are formed with thermal evaporation and lift-off of 100 nm Al layers.

III. RESULTS AND DISCUSSION

A. Electrical characterization of TZO thermistors

A temperature controlled unit with a computer control through a general port interface bus is used to set the measurement temperature and a Keithley 2800 sourcemeter is used to obtain the I–V curve. During the measurement, I–V characteristics of the resistors are acquired while the temperature is continuously swept from 15 to 25 °C (see supplementary material²⁵). TCR is calculated using the following equation:

$$\text{TCR} = \frac{1}{R} \times \frac{\partial R}{\partial T}, \quad (1)$$

where TCR is temperature coefficient of resistance, R is resistance, and T is temperature.

Table II shows the maximum TCR values obtained from the samples. As seen in this table, with the increase in titanium concentration TCR also increases with TZO with 12.2% Ti concentration possessing the highest TCR among the measured films. To investigate the temperature dependent behavior of the TCR, I–V characteristics and the TCR

TABLE II. Maximum TCR values obtained from samples.

Sample	Ti concentration (%)	Maximum TCR values (%/K)
1	2.5	−0.45
2	5.9	−1.08
3	12.2	−5.96

of the TZO with 12.2% Ti concentration are plotted with respect to temperature as shown in Fig. 3 (see supplementary material²⁵). The TCR is observed to lie between −5 and −6%/K from 15 to 22 °C. Moreover, the TCR of pure ZnO thin films grown at 200 °C with the ALD method were reported earlier and are shown to be as low as −0.05%/K (Ref. 10), and pure TiO₂ thin films grown at 200 °C have the maximum TCR of −2.5%/K (Ref. 14) in the temperature range of the current work, which are considerably less than that of the TZO films proposed in this study. ZnO, when deposited at 200 °C, was shown to have a resistivity of 0.015 Ω cm,²⁴ which makes it behave like a very highly doped (unintentional) semiconductor, thereby having low TCR values. TiO₂ grown at 200 °C, on the other hand, has high resistivity, which results in the moderate TCR values in this material. Offering thin films with moderate resistivity levels, which yields higher and more stable TCR values than their pure forms, digital alloying of ZnO and TiO₂, therefore,

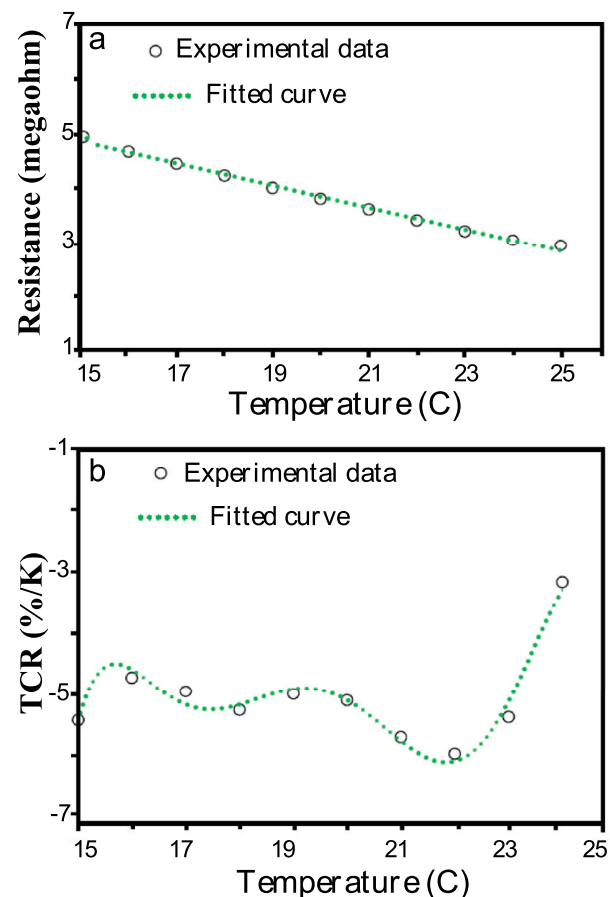


FIG. 3. (Color online) Temperature dependent (a) I–V characteristics and (b) TCR of the TZO film with 12.2 Ti concentration.

presents a promising method for obtaining high performance microbolometer active layers.

IV. SUMMARY AND CONCLUSIONS

In this study, digital alloying of ZnO with TiO₂ (TZO) by atomic layer deposition is explored for the potential of the TZO films as the active material of the uncooled low-cost microbolometers. Three different concentrations of Titanium are investigated and it is demonstrated that the crystalline structure gets distorted with the increase in the Ti concentration. Finally, the TCR of the samples are acquired and the films with 12.2% Ti concentration are shown to possess higher TCR than that of the commercially available active materials. At the same time, the TCR of the same sample is observed to be temperature insensitive in the measurement range between 15 and 22 °C. In conclusion, TZO alloys are shown to have a strong potential to be utilized in future uncooled bolometers in their active layers.

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²⁵See supplementary material at <http://dx.doi.org/10.1116/1.4976513> for XPS studies of TZO films with 5.9% and 12.2% Ti concentration. I-V characteristics of TZO films with 2.5%, 5.9%, and 12.2% Ti concentration. Fit function of temperature dependent TCR curve of TZO film with 12.2% Ti concentration.